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Final Report

TROPHIC TRANSFER OF ATMOSPHERIC AND SEDIMENTARY CONTAMINANTS INTO GREAT LAKES FISH: CONTROLS ON ECOSYSTEM-SCALE RESPONSE TIMES

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Trophic Transfer of Atmospheric and Sedimentary Contaminants into Great Lakes Fish: Controls on Ecosystem-Scale Response Times

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Period Covered by Report:	9 December 1996 - 12 November 2000
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Objectives of the Research Project

During the past two decades, inventories of persistent, bioaccumulative organic contaminants have decreased dramatically in the Great Lakes ecosystem, clearly demonstrating the effectiveness of regulatory decisions about the production and use of certain classes of industrial and agricultural chemicals. For example, concentrations of polychlorinated biphenyls (PCBs) decreased in Great Lakes surface waters (Jeremiason *et al.*, 1994), surficial sediments (Golden *et al.*, 1995; Wong *et al.*, 1995) and fish (Rodgers and Swain, 1983; Miller *et al.*, 1992; DeVault *et al.*, 1988; Baumann and Whittle, 1988) during the 1970's and early 1980's in response to a restriction on PCB production in 1971. Initial rates of decline of PCBs in the Great Lakes were rapid during the 1970's and early 1980's, with pseudo first order rate constants of 0.2 $year^{-1}$ for Lake Superior surface waters (Jeremiason *et al.*, 1994) and ranging for fish from 0.058 (Lake Ontario lake trout; Borgmann and Whittle, 1991) to 0.47 $year^{-1}$ (Lake Michigan coho salmon; DeVault *et al.*, 1988). Clearly, the Great Lakes ecosystem responded favorably and, in retrospect predictably, to decreased loadings of PCBs. Unfortunately, the rate of decline in PCB levels in the Great Lakes ecosystem has apparently slowed during the second half of the 1980's (Baumann and Whittle, 1988) and the most recent data shows little or no change in PCB levels in the Great Lakes fishery (Stow *et al.*, 1995). This apparent stabilization of PCB levels near the FDA advisory level (2 μg/g-wet tissue) is problematic for Great Lakes water quality managers. On one hand, the persistence of PCBs in Great Lakes fish has led to the call for additional regulations, as embodied in the Great Lakes Water Quality Guidance (Federal Register, 1993). Others have argued that the decrease in the rate of recovery of PCBs in the Great Lakes is a natural consequence of internal recycling and continental-scale atmospheric exchange, and that further regulations are neither cost-effective or warranted (Smith, 1995).

The purpose of this study is to quantify the absolute and relative magnitudes of PCB transfers into the Great Lakes fisheries from three exposure routes: (1) atmospheric deposition transferred through the pelagic food web; (2) atmospheric deposition transferred, *via* rapidly-settling particles, through the benthic food web, and; (3) transfer from historically-contaminated, in place sediments through the benthic food web. The approach is to use stable isotopes and PCBs as tracers of carbon and bioaccumulative contaminants, respectively, through the water column and food web of Grand Traverse Bay, an embayment of Lake Michigan. We hypothesized that each of these three routes differ both in their efficiencies of contaminant transfer and in their characteristic response times. This study results in a quantitative, process-driven model of contaminant transfers in the Great Lakes food webs that distinguishes between 'new' (*i.e.*, regional atmospheric deposition) and 'in-place' (*i.e.*, recycling from contaminated sediments) sources of contaminants that support the slowly-changing contaminant inventories in the highest trophic levels of the Great Lakes.

The overall objective of this study is to quantify the absolute and relative flows of bioaccumulative organic contaminants through the pelagic, epi-benthic, and benthic food webs of the northern Great Lakes. We hypothesized that efficient scavenging of atmospheric-derived contaminants from surface waters delivers large chemical fluxes seasonally to the epi-benthic food web, and that this process 'pumps' recent atmospheric loadings into the Great Lakes fisheries. Specific objectives are:

1. To quantify the fluxes of organic carbon on a seasonal basis and associated contaminants from the surface waters to near the sediment-water interface. *Sequencing sediment traps were deployed below the thermocline and near the lake floor to collect settling particles for chemical characterization.*

2. To quantify trophic transfers of carbon and PCBs through the pelagic, epi-benthic, and benthic foodwebs, with emphasis on (1) the episodic deposition of particles to the benthic environment in the spring, and (2) the relative importance of infauna, amphipods, and mysids in contaminant transfer to Great Lakes fish. *Sculpins, macrozooplankton, and infaunal organisms were collected seasonally and analyzed for gut contents, stable isotope composition, and organic contaminant levels. In addition, other epi-benthic and pelagic fish were analyzed periodically.*

3. To quantify, through statistical analysis of contaminant 'fingerprints' and bioenergetics modeling, the relative magnitudes exposure of sedimentary- and atmospherically-derived contaminants to the Great Lakes fisheries. *Principal components analysis are used to compare the PCB congener distributions in water, settling particles, sediments, and biota. A bioenergetics model of the benthic food web is being developed to estimate transfer of carbon from infaunal organisms and settling particles.*

The overall strategy of this field study was to characterize the temporally variable settling flux of organic matter and chemical contaminants from surface waters in the northern Great Lakes and to assess the impact of this flux on carbon and contaminant flows through the benthic food web. Stable isotopes of carbon and nitrogen combined with classical gut content analysis of epi-benthic fishes were be used to characterize the benthic food web. Polychlorinated biphenyl congeners were studied as representatives of the larger class of bioaccumulative organic contaminants and as important pollutants in their own right. This study was conducted in Grand Traverse Bay, a deep,

oligotrophic embayment of Lake Michigan that provides both typical northern Great Lakes conditions and logistical convenience.

Summary of Findings

Finding 1. Episodic Particle Dynamics Control Contaminant Cycling in the Great Lakes.

Prior to this effort, there was no sediment trapping done in Grand Traverse Bay, thus we relied on our 15-year record of sampling in reasonably similar environments for selecting locations for trap placement. Long-term average mass fluxes measured from 1978 to 1992 at a 100 m deep station, 25 km offshore in southeastern Lake Michigan exhibit profiles of mass flux with an exponential increase toward the bottom. From late December through early June, Lake Michigan is virtually isothermal and well mixed. Average fluxes during this period are high through-out the water column, but there is clear evidence of a benthic nepheloid layer (BNL). During the stratified period (June-December),the upper half of the water column becomes isolated from the large inventory of materials in the sediments, although episodic mixing does occur during upwellings. A BNL is still clearly evident from the mass flux profile.

In early May 1997 profiles of non-sequencing traps (4 " diameter)were deployed at stations 6, 8, and 9, along with profiles of sequencing and non-sequencing traps at stations 4, 5, and 7. The primary objective of this extensive sampling was to get some preliminary flux data from a system where none had been previously collected. The non-sequencing trap arrays at stations 6, 8, and 9 were retrieved and redeployed after the onset of thermal stratification, approximately 40 days after deployment, and mass fluxes calculated. All traps were retrieved in mid-September, and sequencing traps were redeployed at stations 5 and 7. Subsamples were distributed for constituent analysis. Measured fluxes for the unstratified May- June period at stations 6, 8, and 9 were low compared to open Lake Michigan values (average 5 g/m^2 -d near the surface),and appeared more like open lake flux profiles during the stratified period when the lake is decoupled from sediment resuspension. All of the profiles exhibit the exponential increase in mass flux near the bottom observed in all Great Lake profiles and attributed to a benthic nepheloid layer. The samples from trap 6 exhibit a peculiar profile --some sample was lost from the bottom trap during retrieval in June, but the low flux values at 75 m are unexplained at this time. The sequencing trap mass flux values from relatively shallow (45 m) station 4 were unexpectedly low for the entire spring-summer period. The three samples immediately after the onset of stratification were the highest recorded for the entire period of deployment and will be examined for biogenic silica. This may be the spring bloom in the southeastern portion of the bay. There was a small peak in mass fluxes at the near-surface of station 5 and 7 in late spring, but except for the initial interval immediately after deployment, the qualitative pattern of mass fluxes were not synchronous within the eastern arm of the bay. Near-bottom fluxes were several times higher at station 7 than at station 5 and may point to a region of sediment focusing near station 7.

Two sequencing traps were deployed in mid-September 1997 at station 5 (30 and 91 m)and three at station 7 (15, 30, and 115 m). Trap sampling intervals were set at 15 days. These stations were selected by collaborators as the primary water column stations and were sampled approximately monthly during the 1997-98 season. These traps were retrieved and others redeployed at 30 m below the surface at stations 5, 7, 8, and 9 in early September 1998. These final deployments had

collection intervals of 12-15 days and were retrieved in early August 1999. These deployments have provided 2 complete years of mass fluxes and samples for analyses from 30 m below the surface at stations 5 and 7 in the eastern and nearly 1 full year from the same depth in the western arm (station 9). There is clear evidence in these records of strong resuspension during the unstratified periods in the 2 years. These fluxes are substantially higher at the more southern station (5) than at station 7. The qualitative flux patterns do not appear to be well synchronized between these two stations implying a complex transport of particulate matter within the western arm of the bay. Peak mass fluxes at station 9, in the eastern arm, are about the same magnitude during the unstratified period, but not well correlated temporally. Our results clearly support the hypothesis that there is significant sediment-water exchange of chemical constituents during the unstratified periods when massive sediment resuspension events occur.

The stable isotopic composition of suspended particles varied substantially vertically and seasonally, with $\delta^{13}C$ values ranging from -30.7 to -23.9‰. Low $\delta^{13}C$ values that occur concurrently with a peak in fluorescence below the thermocline reflect uptake of ^{13}C depleted respiratory CO_2 and/or the accumulation of ^{13}C depleted lipids by phytoplankton. High $\delta^{13}C$ values late in the season likely result from a reduction in photosynthetic fractionation associated with a decrease in the CO_2 pool. Seasonal $\delta^{15}N$ values of suspended particles reflect a balance between fractionation during assimilation of NH_4^+ or NO_3^- and degradative processes.

The total polycyclic aromatic hydrocarbon (*t*-PAH) and total polychlorinated biphenyl (*t*-PCB) settling fluxes to the surface waters in the southern site were significantly greater than those from the northern site. In addition, there were more frequent brief increases in the mass flux to the southern site than to the northern site. These episodic events, which occurred only 20% of the time, accounted for 65% of both the mass flux and *t*-PAH flux. The *t*-PCB flux was not influenced by these episodic events and only 18% of the *t*-PCB flux occurred during these events suggesting that *t*-PAHs are a better tracer of particle dynamics than *t*-PCBs. Several large mass flux events characteristic of seiches were observed simultaneously in the benthic nepheloid layer (BNL) at both the northern and southern site. The particles settling during the resuspension events had lower *t*-PCB and *t*-PAH concentrations than particles settling at other times. This suggests that the material settling into the traps on the high mass flux days is composed of a mixture of the less contaminated underlying sediment and the "regular" contaminant rich particles settling into the BNL.

Sediment cores were collected from two sites in Grand Traverse Bay, Lake Michigan in May 1998, dated using ^{210}Pb geochronology, and analyzed for polychlorinated biphenyl congeners, polycyclic aromatic hydrocarbons, and toxaphene. The extraordinarily high sediment focusing and accumulation rates in these cores relative to other Great Lakes sediments, allowed quantification of high resolution temporal trends in the burial of hydrophobic organic contaminants. The surficial focus-corrected accumulation rate of total PCBs (sum of 105 congeners) was 0.50 ng/cm^2-year at both sites. Toxaphene and total PAH (sum of 33 compounds) surficial accumulations varied at each site and ranged from 0.08 to 0.41 ng/cm^2-year for toxaphene and 25 to 52 ng/cm^2-yr for tPAHs at the two sites. The maximum *t*-PAH accumulation rate was in sediment dated from 1942 and PAH accumulation decreased from 1942 to 1980 with a first order rate of decline 0.017 yr^{-1}. Both toxaphene and *t*-PCB accumulations peaked in sediment deposited in 1972, after which their accumulation decreased with a rate of decline of 0.027 yr^{-1} and 0.028 yr^{-1} respectively.

What is the relative importance of 'new' (*e.g.*, diffuse non-point source atmospheric deposition) versus 'historical' (*e.g.*, in place contaminated sediments) loadings of persistent bioaccumulative toxins in supporting PBT levels in Great Lakes fish? Two independent lines of evidence suggest that current exchange of PBTs between the Great Lakes and the atmosphere are quantitatively more important than remobilization of PBTs from deep-water sediments: (1) as shown in this study, detailed analysis of the seasonal variations in PBT flows, carbon and particle transport, and food web dynamics, indicates that organic-rich, PBT-laden settling particles supply chemicals to epi-benthic fishes; (2) our further analysis of PBT levels in Great Lakes fish and water, made possible by this study, expend the long term record and allow us to examine the temporal trends in each media. As discussed below, this analysis indicates that the PCB levels in the Great Lakes air, water, and biota are declining at remarkably similar rates, suggesting a tight coupling. In contrast, PCB levels in surficial sediments are declining more slowly due to mixing of historically-deposited contaminants from deeper sediments.

Finding 2. Trophic Transfer of Persistent Bioaccumulative Toxins Reflects Recent Atmospheric Loadings.

Representative food web members were collected monthly from Grand Traverse Bay, Lake Michigan between April 1997 and September 1998 to quantify PCB and toxaphene biomagnification and to examine the primary variables responsible for elevated concentrations in predatory fish. Samples were separated by species, month, and length, and analyzed for lipid content and the organochlorine contaminants PCBs and toxaphene. Sub-samples of biota were analyzed for the stable isotopes of nitrogen and carbon to aid in establishing trophic structure of the food web. Both PCB and toxaphene levels were lowest in the invertebrate shrimp *Mysis relicta* and highest in the benthic fish burbot (*Lota lota*). A significant correlation between length and contaminant concentration was only observed in deepwater sculpin (*Myoxocephalus thompsoni*). Nitrogen isotopes were confounded by multiple variables in this system, particularly seasonal variation, and did not display a simple pattern of enrichment among trophic levels. However, $\delta^{13}C$ displayed little seasonal variation and was positively correlated with PCB concentrations among food web members (r^2= 0.69). Plots of $\delta^{13}C$ vs. PCBs separate food web members into three distinct groupings, comprised of invertebrate grazers, primary forage fish, and predatory fish. Stable isotopes analysis was also performed on the primary organic sources, suspended solids, settling particles, and sediment. A regression analysis conducted between seasonally adjusted $\delta^{15}N$ and lipid normalized PCB concentrations, including all food web members and primary organic sources, indicates that there may be two sources of contaminants to the food web. Suspended particles deliver PCBs to pelagic food web members and species that receive a majority of their nutrition through pelagic sources. Settling particles are more refractory in nature and supply PCBs to benthic food web members and *Mysis relicta*.

Seasonal variations in PCB and toxaphene burdens were measured in bulk zooplankton, *Mysis relicta, Deparia hoi, Alosa pseudoharengus,* and *Coregonus hoi* collected from Grand Traverse Bay, Lake Michigan between April and September of 1997 and 1998. Seasonal changes were most pronounced in zooplankton, which displayed highest PCB burdens in April and decreased by as much as 75% through September, coincident with changes in phytoplankton biomass, species composition, and changes in the particulate pools of PCBs in the water column. *Mysis* sp. display a similar PCB trend as zooplankton, although not as extreme, while *Deparia* sp. displayed maximal

PCB concentrations in August of 1997. Similarities and trend between water column HOC pools and biota HOC burdens became dampened higher in the food chain. PCB trends in the primary forage fish alewife (*Alosa pseudoharengus*) and bloater (*Coregonus hoi*), were correlated more to shifts in lipid content and diet changes seasonally. PCB concentrations were higher ($p<0.01$) in bloater (310 ± 98 ng/g wet weight) than alewife (233 ± 70 ng/g wet weight), however alewife possessed higher toxaphene burdens (198 ± 72 ng/g wet weight) than bloater (88 ± 36 ng/g wet weight). Alewife contaminant burdens were high in spring and fall of both years, decreasing by as much as 60% in mid-summer, and were reflective of changes measured in their lipid content associated with gamete production and over-wintering storage. Bloater contaminant burdens were relatively consistent throughout the season. However, the highest measured concentrations of PCBs in bloater were observed in June of both years coincident with shifts in their diet.

Finding 3. PCB Inventories in Great Lake Compartments are Declining at Similar Rates.

Nearly two decades of research has shown that atmospheric deposition in general, and gas exchange in particular, are important geochemical pathways controlling the levels of PCBs in the Great Lakes. Absorption of gaseous PCBs from the atmosphere and volatilization of dissolved PCBs from surface waters are relatively rapid processes, resulting in facile exchange between these two contaminant reservoirs. Rather than thinking of atmospheric deposition as a 'pipe' delivering PCBs and other semivolatile chemicals to the lakes, it is better to view the current situation as two large reservoirs (air and water) which rapidly exchange contaminants. This conclusion is based on current estimates of gas exchange fluxes and PCB inventories in the water in air. This facile exchange implies that spatial and temporal dynamics in PCBs in the water should be reflected in parallel dynamics in the atmosphere, and *vice versa*. To test this hypothesis, we now examine the coincident changes in PCBs levels in various Great Lakes compartments.

The Great Lakes region is blessed with one of the best long-term records of PCB levels in air, water, sediment, and biota in the world. Analytical methods have been developed, refined, and standardized among research and government laboratories, allowing for data to be directly compared. Highly-sensitive, congener-specific methods have been applied to air and water from the open Great Lakes since the mid-1980's. Fish tissue samples have been collected and analyzed for PCBs in a consistent manner since the early 1970's. These data provide a unique opportunity to quantify the response of the ecosystem to a specific management action (the banning of PCB production), to calibrate our understanding of PCB cycling in the Great Lakes, and to evaluate future PCB levels.

To test the hypothesis that facile air-water exchange couples PCB inventories in the atmosphere and surface waters, we examine whether these inventories are changing in time in a similar way. Smith (2000) has recently conducted a similar analysis for Lake Superior PCB data–here we build upon Smith's work by adding additional data and extending the data to Lake Michigan. Here we consider the coincident rate of change in PCB concentrations in six Great Lakes media–air, surface waters, settling particles, accumulating bottom sediments, gull eggs, and lake trout. Average annual total PCB concentrations (or accumulation rates for sediments) were calculated from the data in the literature for each media. The data used includes that summarized by Smith (2000) for Lake Superior, ambient gas phase PCBs measured by the Integrated Atmospheric Deposition Network (IADN) and by our work in northern Lake Michigan, surface water PCB levels in Lake Michigan summarized by Offenberg and Baker (2000) extended with recent

measurements in Grand Traverse Bay, Lake Michigan, and settling particles from Lake Superior (1984, 1987, 1991) and Grand Traverse Bay (1998) surface waters. Temporal trends in PCB burial in sediments is estimated by a radiodated sediment core from Grand Traverse Bay. Gull egg PCB data are from two nesting colonies in Lake Superior measured by the Canadian Wildlife Service, and lake trout are from the EPA sampling program in Lake Michigan, augmented by our recent measurements in Grand Traverse Bay. A simple first order model was then used to calculate the rate of PCB decline and the corresponding half-life in each media. Results are shown in Figure 3 and summarized in Table 1.

This analysis shows that the PCB levels are declining in all six Great Lakes media, and that the declines approximately follow first order kinetics, as expected in response to reduced external loadings. Interestingly, the rate of decline is within 40% between PCBs in the air and surface waters. During the period between 1986 and 1998, the average concentration of PCBs in the water (ng/L) equaled 1.5 times the concentration in the air (ng/m^3), or the effective dimensionless Henry's Law constant was 7 x 10^{-4} (Figure 4). PCB levels in both the air and surface waters are decreasing with a half-life of 5-7 years, suggesting a relatively rapid response for these large environmental reservoirs. Interestingly, PCBs are declining in biota at comparable rates as the declines observed in the air and surface waters, with half-lives ranging from 5 years for lake trout to 9 years in gull eggs. While certainly an indirect argument, this synchronicity in PCB response rates suggests a close coupling between air, water, and Great Lakes biota.

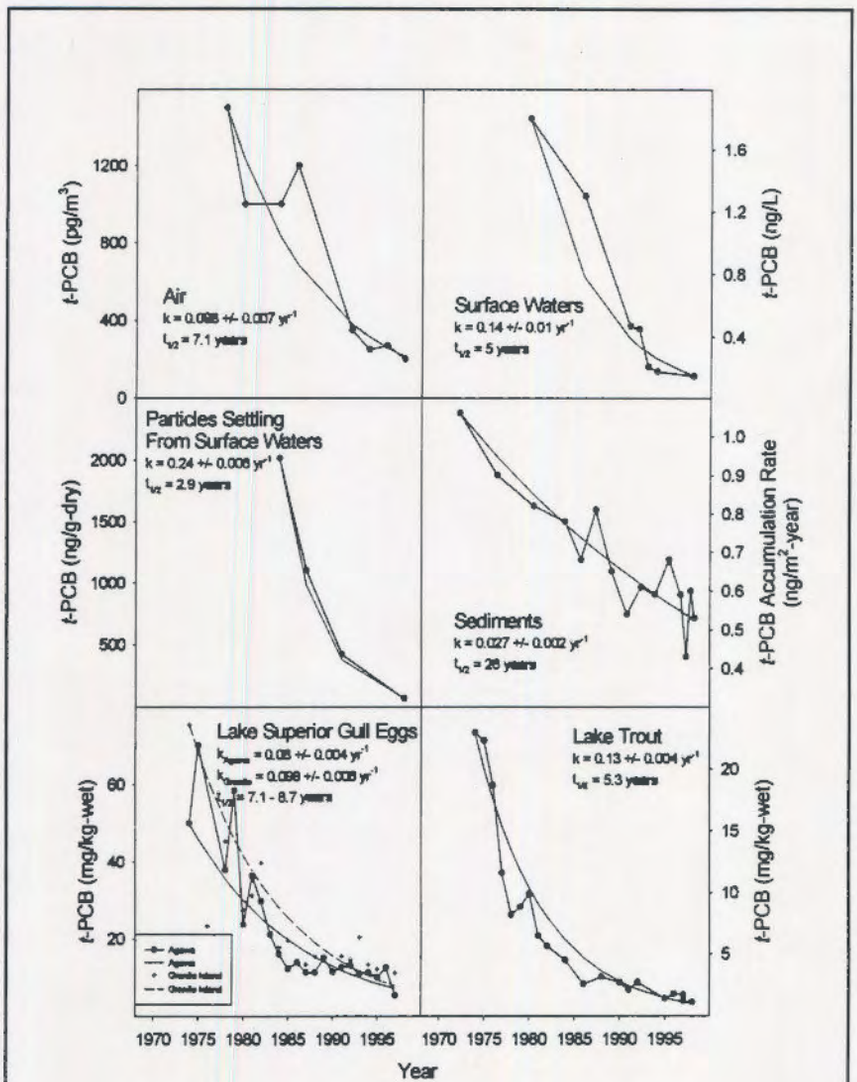

Figure 1 Temporal trends in PCB levels measured in Lakes Superior and Michigan during the past twenty years.

Table 1. Summary of first order PCB decreases in Lake Michigan and Superior air, water, sediments, and biota.

Lake Michigan/ Superior Media	Period Used for Trend Analysis	First Order Loss Rate (yr^{-1})	Half Life (years)
Air	1986-1998	0.1±0.01	7
Surface Waters	1980-1998	0.14±0.01	5
Settling Particles	1984-1998	0.24±0.006	2
Accumulating Sediments	1972-1998	0.027±0.002	26
Gull Eggs - Agawa	1974-1997	0.08±0.004	9
Gull Eggs - Granite	1974-1997	0.1±0.006	7
Lake Trout	1974-1998	0.13±0.004	5

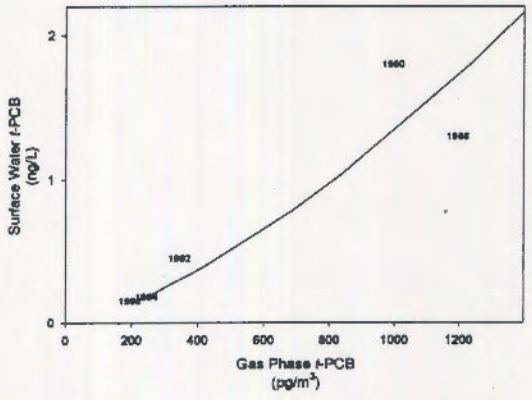

Figure 2 Relationship between annual average total PCB concentrations in Lake Michigan air and surface waters.

It is interesting to note that the PCB response rate in accumulating sediments is 4-5 times slower than those observed in biota. This slower response in sediments is likely due to mixing of more highly contaminated sediments from depth into the overlying sediment layers, in effect dampening the response seen in the other compartments. The observation that PCB levels in biota are tracking the temporal responses seen in air and water suggests to us that PCB burdens in Great Lakes biota are supported by exposure in the water column rather than by recycling of contaminated sediments.

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Relevant Web Sites

www.glerl.noaa.gov (access to Chapter 2)

ftp://ftp.glerl.noaa.gov/publications/tech_reports/glerl-116 (access to sediment trap and physical limnology data from this study)

www.cbl.umces.edu/~baker (access to data archives for this study)

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CHAPTER 2

Settling Particle Fluxes, and Current and Temperature Profiles in Grand Traverse Bay, Lake Michigan

Brian J. Eadie, Gerald S. Miller, Margaret B. Lansing, and Andrew G. Winkelman

NOAA Technical Memorandum GLERL-116

SETTLING PARTICLE FLUXES, AND CURRENT AND TEMPERATURE PROFILES IN GRAND TRAVERSE BAY, LAKE MICHIGAN

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Settling Particle Fluxes, and Current and Temperature Profiles in Grand Traverse Bay

Brian J. Eadie
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Abstract. Settling particle fluxes and mass flux profiles are reported for trap samples collected at five stations in Grand Traverse Bay, Lake Michigan during 1997-1999. Trap collection precision is estimated, and 10 cm and 20 cm diameter sequencing traps are inter-calibrated using data from traps deployed in replicate on specially constructed brackets. Temperature data is reported for two stations (during June-September 1997). Acoustic Doppler Current Profilers (ADCP) current meter data and contours of backscatter strength, U and V current components, and water temperature are included for the 95 m station. All data is available online in ASCII and MS Excel formats at ftp://ftp.glerl.noaa.gov/publications/tech_reports/glerl-116.

INTRODUCTION

In 1997 the EPA-Ecological Assessment Program funded a 3-year coordinated proposal from GLERL, the University of Maryland, and Michigan State University whose overall objective was to quantify the absolute and relative flows of bioaccumulative organic contaminants through the pelagic, epi-benthic, and benthic food webs of Grand Traverse Bay in northern Lake Michigan. We hypothesize that efficient scavenging of atmospheric-derived contaminants from surface waters delivers large chemical fluxes seasonally to the epi-benthic food web, and that this process pumps recent atmospheric loadings into the Great Lakes fisheries. Specific objectives, with abbreviated approaches in italics, were:

1. To quantify the seasonal fluxes of organic carbon and associated contaminants from the surface waters to near the sediment-water interface. *Sequencing sediment traps will be deployed below the thermocline and near the lake floor to collect settling particles for chemical characterization.*

2. To quantify trophic linkages in the epi-benthic food web, with emphasis on the relative importance of seasonally-dependent settling fluxes from surface waters and ingestion of infaunal organisms. *Sculpins and other epi-benthic fishes, macrozooplankton, and infaunal organisms collected seasonally will be analyzed for gut contents, stable isotope composition, and organic contaminant levels.*

3. To quantify, through statistical analysis of contaminant fingerprints and bioenergetics modeling, the relative magnitudes exposure of sedimentary- and atmospherically-derived contaminants to the Great Lakes fisheries. *Principal components analysis will be used to compare the PCB congener distributions in water, settling particles, sediments, and biota. A bioenergetics model of the benthic food web will be used to estimate transfer of carbon from infaunal organisms and settling particles.*

The overall strategy of this field study was to carefully characterize the settling flux of organic matter and chemical contaminants from surface waters during three seasons in the northern Great Lakes and to assess the impact of this flux on carbon and contaminant flows through the benthic food web. Stable isotopes of carbon and nitrogen combined with classical gut content analysis of epi-benthic fishes are being used to characterize the benthic food web. Polychlorinated biphenyl congeners are being studied as representatives of the larger class of bioaccumulative organic contaminants and as important pollutants in their own right. This study has been conducted in Grand Traverse Bay (Figure 1), a deep, oligotrophic embayment of Lake Michigan that provides both typical northern Great Lakes conditions and logistical convenience.

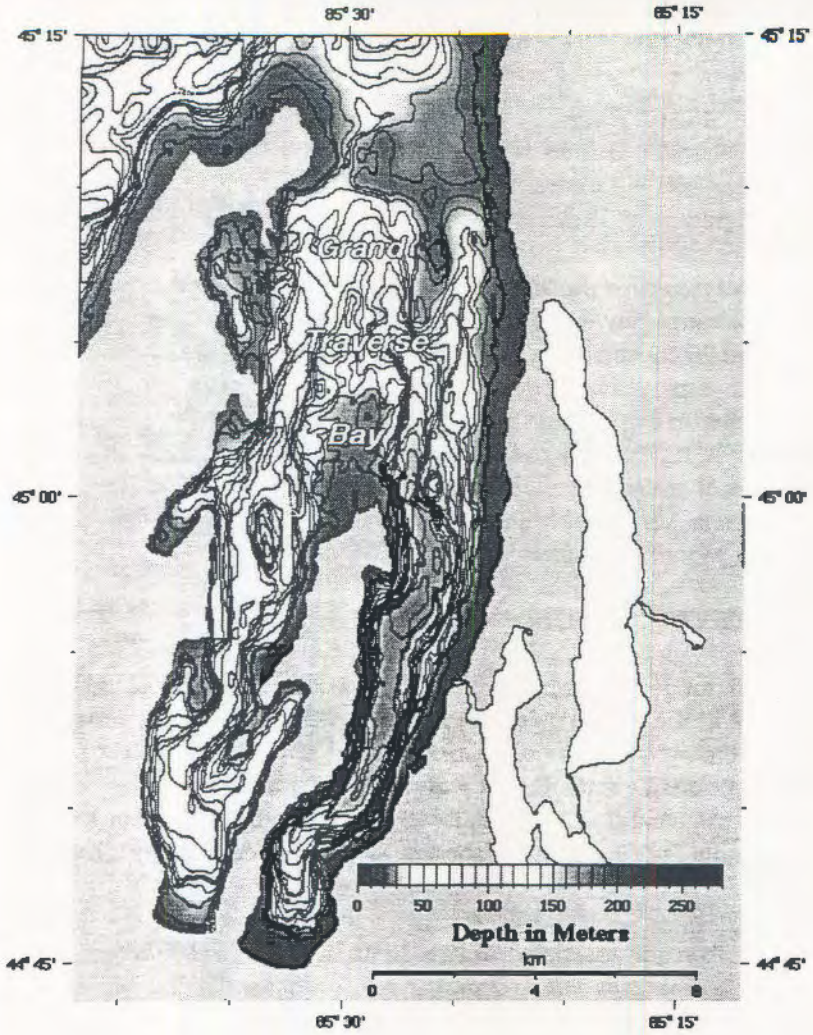

Figure 1. Bathymetry of Grand Traverse Bay (Holcombe, et al., 1996)

For many constituents in the Great Lakes, the resuspension of surface sediments, (which contain large inventories of certain nutrients and contaminants deposited over the past few decades) presently results in much greater fluxes than from external inputs (Eadie et al., 1984, 1989; Eadie and Robbins, 1987; Robbins and Eadie, 1991; Brooks and Edgington, 1994). For example, Lake Michigan is the sixth-largest lake in the world and has a hydraulic residence time of about 62 years (Quinn, 1992). For particle-reactive constituents, internal removal through sedimentation is much more rapid than this. Radiotracer studies with ^{239}Pu ($t_{1/2}$ = 25,000 years) and ^{137}Cs ($t_{1/2}$ = 30.2 years) show that >95% of these tracers were removed from the water and transferred to sediments within a few years (Wahlgren et al., 1980; Eadie and Robbins, 1987). Although initial removal of particle-reactive tracers from the water is rapid (a few years), a small residual concentration remains in the water (either on particles, in biota, or in solution) and now diminishes exponentially on a time scale of decades. Studies of Thomann and DiToro (1983), Eadie et al. (1984), and Robbins and Eadie (1991), have shown that the small amount remaining in the system is primarily the result of an annual cycle of sediment resuspension and redeposition that releases constituents from sediments back into the water. The long-term decline of ^{239}Pu and (decay-corrected) ^{137}Cs in the lake has about a 20-year time constant (Wahlgren et al., 1980), which probably characterizes the net rate of incorporation of these tracers into permanent sediments (Robbins, 1982).

The processes of particle flux and resuspension has been examined in Lake Michigan through the use of sediment traps since the mid 1970s (Wahlgren et al., 1980; Eadie et al., 1984). These cylindrical devices are moored at

selected depths to intercept materials settling to the bottom. Traps provide an efficient tool for the collection of integrated samples of settling materials for detailed analysis. Measuring the mass collected allows us to calculate the gross downward flux of particulate matter and associated constituents and to calculate both mass and constituent settling velocities.

GLERLs primary role in the study was to provide expert sampling advice, to collect settling materials using our autosequencing sediment traps and provide subsamples to co-investigators for constituent analysis, and to participate in the ultimate analysis of all of the data collected in the project. During the summer of 1997, GLERL needed to test two new Acoustic Doppler Current Profilers (ADCP) and these, along with temperature recording equipment, were deployed in the western arm of the bay providing several months of data where no other current data were available.

METHODS

Two types of sediment traps were used in this study. Our simple trap, based on reviews of various designs (Bloesch and Burns, 1980; Gardner, 1980a,b), is a cylinder 10 cm in diameter with an aspect ratio of 5:1 above the funnel opening to a 500 ml polyethylene bottle. In 1990 we developed a sequencing trap modified from the designs of Baker et al. (1988), and Jannasch et al. (1980). These are also cylindrical, but with an inner diameter of 20 cm and an aspect ratio of 8:1 above the funnel. A computer-controlled carousel contains 23 polyethylene bottles (60 ml), which rotate under the funnel at preprogrammed intervals. An electric motor rotates the carousel and uses a single-pole detent switch to provide position feedback. A microprocessor-based controller, developed in house, runs the motor based on a schedule and records confirmation of each rotation using nonvolatile memory. A battery pack allows up to 2 years of operation. Cylindrical traps have a high collection efficiency in low current lake environments and have proved satisfactory in many lake studies (Bloesch and Burns, 1980; Eadie et al., 1984). The accuracy of calculated fluxes is poorly understood, but depends on the trap design, the types of particles in the fluid, and the currents at the site (Gardner, 1980b; Hawley, 1988; Gardner, 1996).

Trap Sampling Precision: To estimate trap collection precision and intercalibrate between the 10 cm diameter traps and the 20 cm diameter sequencing traps, a series of deployments were made between 1984 and 1989 in regions with a wide range of fluxes on specially constructed brackets to assure identical depth and exposure. The 20 cm traps used in these tests did not have sequencing capability, but were identical in other aspects. The traps were deployed as anchored arrays using subsurface buoyed 1/4" steel cable. The 500 ml bottles in the simple traps were poisoned with 25 ml of chloroform and filled with distilled water prior to deployment. The 60 ml polyethylene collection bottles in the sequencing trap were poisoned with 6 ml of chloroform and filled with distilled water immediately prior to deployment. This concentration of chloroform is an effective preservative (Lee et al., 1989) and results in a supersaturated solution, with beads of chloroform remaining after retrieval. The sequencing traps are deployed with the collection funnel feeding to an empty opening (no collection bottle). After a preprogrammed period of time, the carousel will move the first collection bottle under the funnel. The remaining 22 bottles will follow in a preprogrammed sequence. After retrieval, the sample bottles are removed from the traps and transported to the laboratory in cold storage (4°C). The traps have on-board intelligence that records the time of each sequence and various system checks.

When deployed in replicate, both the 10 cm and 20 cm traps showed good repeatability with paired t-test showing equal means ($P<0.05$) in all four comparisons (Figure 2). The 10 cm traps replicate with an average difference between pairs of ±11%, and the 20 cm traps (with the 8:1 aspect ratio) replicate with an average difference between pairs of ±14%. An intercomparison of capture efficiency between the 10 and 20 cm traps resulted in a design change from an aspect ratio of 5:1 to 8:1 for the larger diameter traps. A larger trap diameter results in a higher trap Reynolds number, with presumably lower collection efficiency. There was little bias (slope = 1.05) between the two types of traps, and the scatter was much reduced with the extended aspect ratio, which became our standard for 20 cm diameter traps. All sequencing traps in this study have an aspect ratio of 8:1.

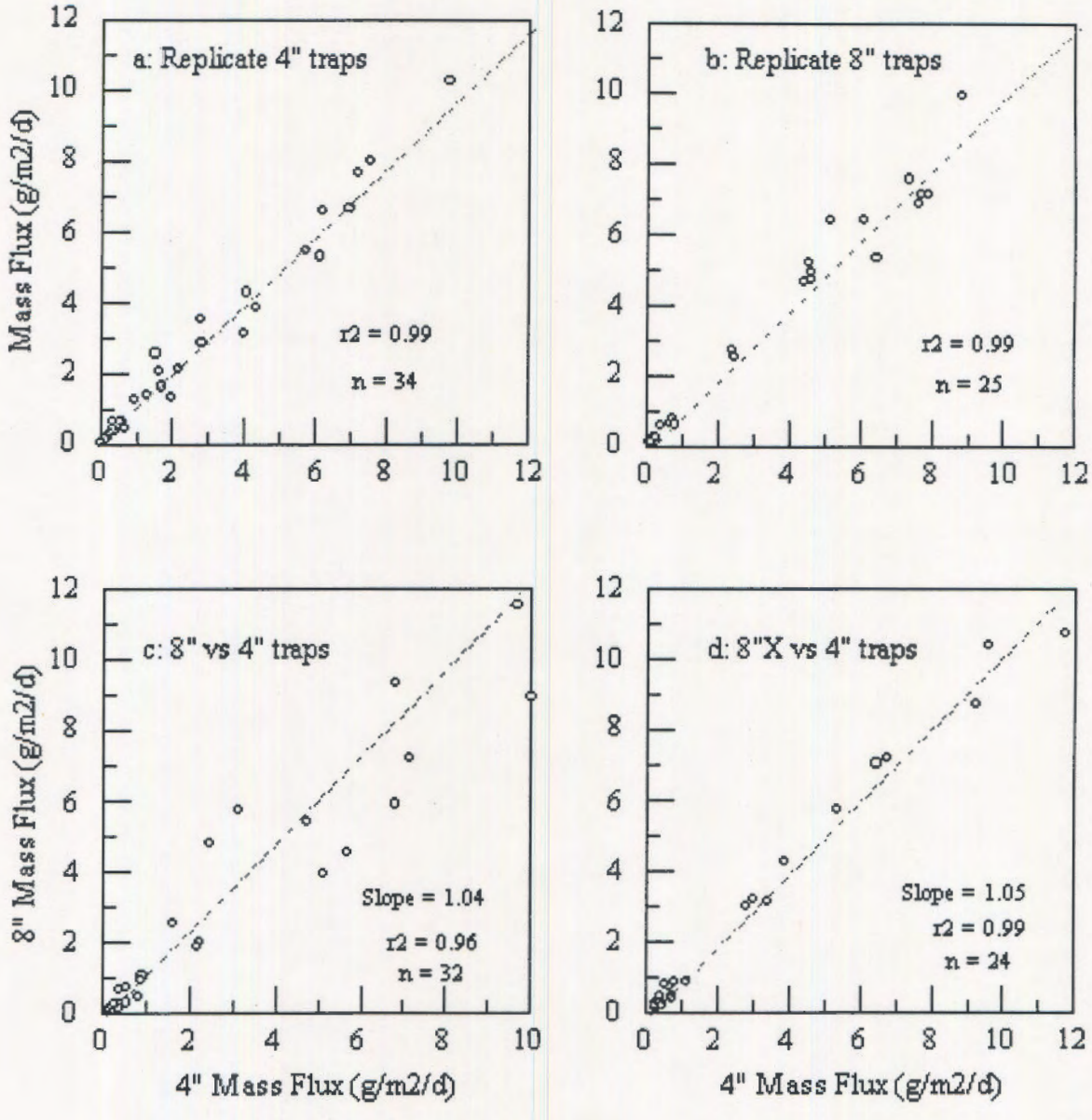

Figure 2. Comparisons of replicate trap flux measurements. (a) Replicate 10 cm (4") diameter traps placed on brackets for simultaneous deployments. Correlation coefficient is high and the traps replicate with an average difference between pairs of ± 11%. (b) A similar treatment of 20 cm (8") diameter traps with similar results. (c) A comparison of 10 cm and 20 cm traps with 5:1 aspect ratios. The scatter was worse than for individual pairs of the same size. (d) Comparison of 10 cm (5:1 aspect) with 20 cm (8:1), extended aspect ratio. There was little bias (slope = 1.05) between these pairs and the scatter was much reduced with the higher aspect ratio.

Sample Handling: After arrival at the lab, the trap samples are allowed to settle in a refrigerator for 1 day, then overlying water is carefully siphoned off and the residual is split into two equal portions. One half of the sample is transferred into a precleaned glass jar and frozen for subsequent PCB analysis. The other half of each sample is freeze dried, then weighed and transferred into precleaned scintillation vials for storage in a freezer. This fraction is used for analysis of nutrients, stable isotopes, etc. All trap samples were weighed on an analytical balance calibrated to within ±1 mg with known standard weights during each weighing session. Flux is equal to the mass collected divided by the length of collection and the trap cross section. To calculate fluxes from the trapped material, a reliable measurement of the total weight is required. In previous studies we always split sediment trap samples after they were freeze dried and weighed.

Because this project involves quantification of PCBs and other trace organic contaminants that require wet extraction procedures, it is necessary to accurately divide the samples into two fractions while still wet. A total weight of the sample can then be estimated from the freeze-dried split of the total material.

After further literature and catalog searches we purchased a stainless steel dry sediment sample micro-splitter (Model SP-241x; Gilson Co. Inc., PO Box 677, Worthington, OH, 43085-0677). This model has a reservoir of approximately 80 ml into which the sample is poured. A bottom vent is then opened, and the sample can be poured into 30 evenly spaced (1 mm) slots. The even numbered slots empty into a stainless steel tray on the left, and the odd numbered slots empty on the right. We then tested this device for our wet sample splitting requirements and came up with the following satisfactory results.

Sample Matrices: Our objective was to determine the precision of splitting and the ratio of the two samples. To do this, four samples were examined:

1. Distilled water (DDW).
2. Distilled water (55 ml) + chloroform (6 ml); our standard trap poison solution.
3. Ground Lake Michigan sediment in #2.
4. A sediment trap sample from Lake Michigan near LMMB station 6; 5 m above bottom from a 100 m deep station.

Five replicates of each matrix were made. The samples were poured into the splitter, and the left and right trays were weighed for matrices 1 and 2. For matrices 3 and 4, the left and right trays were emptied into preweighed beakers that were dried at 90°C then weighed. The data are presented in Table 1.

Excellent replication was obtained in the tests (Table 2). Matrices 3 and 4, with sediment or trap materials, were split into two equal portions without bias. In other studies we have determined that replicate traps placed side by side have a coefficient of variation (100*sd/mean) of a little less than 10%. The splitting errors appear substantially smaller and will not degrade our interpretation of the data.

Our standard splitting procedure is:

1. Allow the 60 or 500 ml trap bottles to settle for approximately 24 hours in refrigeration.
2. Extract approximately 25 ml of the overlying water with a syringe, remove excess overlying water from 500 ml trap bottles.
3. Pour the remaining trap sample through a 500 um (355 um for year 2) screen into the splitter reservoir.
4. Split by opening the bottom valve.
5. Rinse with the water from step #2.
6. Further rinse (if needed) with (CHCl3) pre-extracted DDW.
7. Pour right tray back into trap sample bottle for PCB, etc.
8. Pour left side into pre-cleaned beakers for freeze drying, weighing, and analyses.
9. Transfer >500 um (>355 um for year 2) materials to precleaned, preweighed filters.
10. Rinse screen and splitter under faucet, then rinse with pre-extracted DDW.

Table 1. Sample Splitting Data

	Total Dry Wt (g)	Wt (left) (g)	Wt (Right) (g)	Fract left	Fract Rt
DDW		33.4473	31.4184	0.516	0.484
DDW		32.5575	30.962	0.513	0.487
DDW		32.9653	30.9628	0.516	0.484
DDW		32.2945	29.296	0.524	0.476
DDW		31.7108	29.3542	0.519	0.481
DDW(55):CHCl3(6)		31.6683	33.0099	0.490	0.510
DDW(55):CHCl3(6)		30.2318	31.3103	0.491	0.509
DDW(55):CHCl3(6)		31.2056	31.5524	0.497	0.503
DDW(55):CHCl3(6)		30.8368	31.6704	0.493	0.507
DDW(55):CHCl3(6)		31.0031	33.3368	0.482	0.518
Grnd Sed in DDW(55):CHCl3(6); DRY	0.5639	0.2779	0.286	0.493	0.507
Grnd Sed in DDW(55):CHCl3(6); DRY	1.387	0.6952	0.6918	0.501	0.499
Grnd Sed in DDW(55):CHCl3(6); DRY	2.9349	1.5035	1.4314	0.512	0.488
Grnd Sed in DDW(55):CHCl3(6); DRY	3.9479	1.9049	2.043	0.483	0.517
Grnd Sed in DDW(55):CHCl3(6); DRY	5.1343	2.5843	2.55	0.503	0.497
Trap from 5m AB @ 100m sta.; DRY	0.4434	0.2224	0.221	0.502	0.498
Trap from 5m AB @ 100m sta.; DRY	0.7476	0.367	0.3806	0.491	0.509
Trap from 5m AB @ 100m sta.; DRY	1.2745	0.6423	0.6322	0.504	0.496
Trap from 5m AB @ 100m sta.; DRY	1.3124	0.648	0.6644	0.494	0.506
Trap from 5m AB @ 100m sta.; DRY	2.2998	1.1689	1.1309	0.508	0.492

Table 2. Accuracy and precision of sample splitting (n=5; all mixtures).

Mixture	Left Side Fraction	Right Side Fraction	P (paired t)
DDW	0.518 ± 0.004	0.483 ± 0.004	
DDW + CHCl3	0.491 ± 0.005	0.509 ± 0.005	
Ground Sediment	0.498 ± 0.010	0.502 ± 0.010	0.77
Trap	0.500 ± 0.006	0.500 ± 0.006	0.93

Current and Temperature Measurements

Two current meter/water temperature moorings were deployed 18 June 1997 (Figure 3) in the western arm of Grand Traverse Bay. A 300 kHz RDI Workhorse Acoustic Doppler Current Profiler (WH-ADCP) was moored 9 m below the surface in a downward-looking mode at each site. A 810 mm syntactic foam subsurface buoy, designed for the WH-ADCP, provided about 100 kg reserve buoyancy. Mooring information and ADCP setup parameters are given in Table 3. On the southern mooring, C5, an Aanderaa 40-m thermistor chain measured hourly water temperatures at 4 m intervals from depths of 13 m to 53 m. Five Brancker T-1000 temperature loggers were attached to the mooring line at C7 with a 4 m spacing beginning at -13 m. The ADCPs also measured water temperatures at the transducer head at the 9 m depth. A hardware-limiting problem in both WH-ADCP's resulted in low echo intensities for cell #1 that caused the internal data quality checking routines to reject the velocity data from that cell. At mooring C7, the current and echo electronics in the ADCP failed after 6 days, but the water temperature measurements continued for the entire deployment and are included with the temperature logger data.

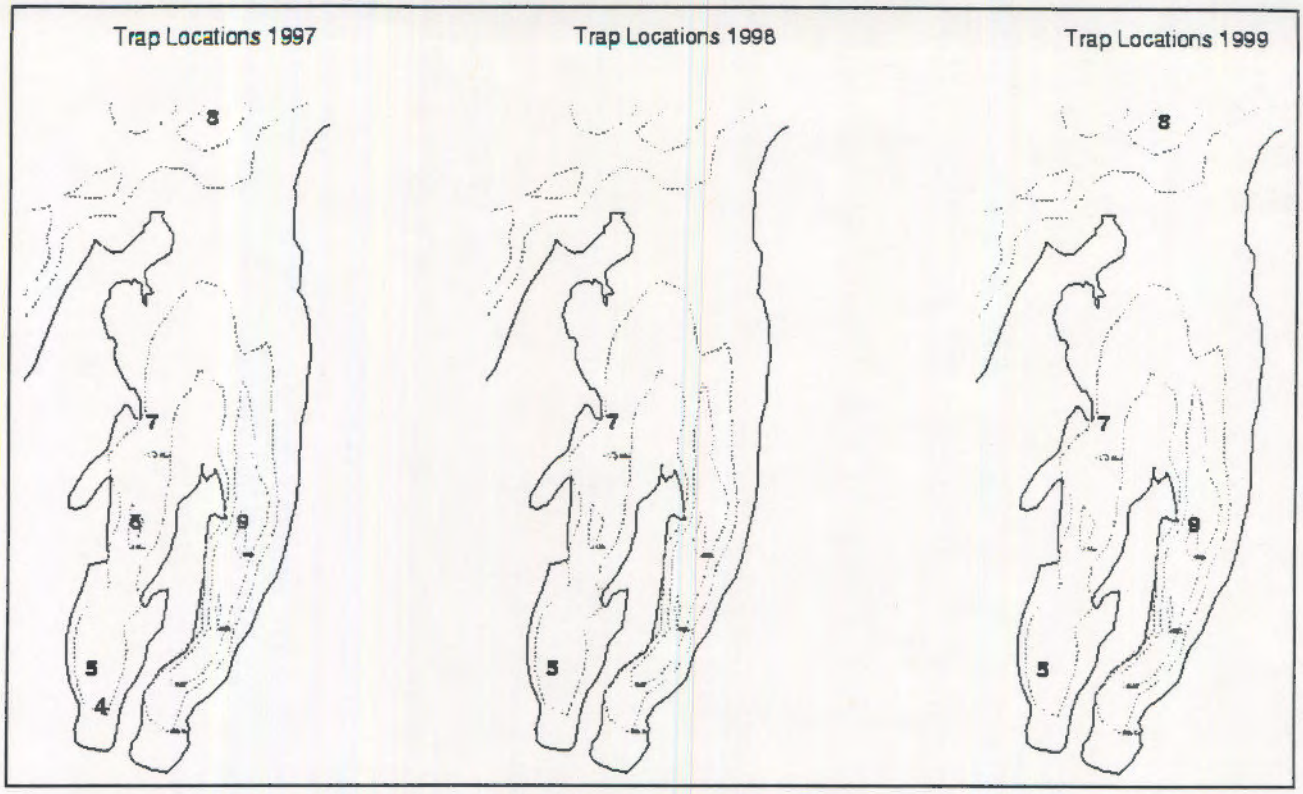

Figure 3. Locations of sediment traps (Station numbers 4-9) and ADCP (stations 5 and 7).

Table 3.--Mooring Information and Acoustic Doppler Current Profiler Setup Procedures.

Moorings	**C5**	**C7**
Location	44°49.39' 85°37.41'	45°01.68' 85°33.05'
Water Depth	94.5 m	118.0 m
Deployed	06/18/97 1030 EST	06/18/97 1300 EST
Retrieved	09/16/97 1700 EST	09/17/97 1100 EST
Current meters:		
ADCP	300 kHz	300 kHz
No. cells	45	55
Cell size	2 m	2 m
# pings	400	400
Std deviation	0.5 cms^{-1}	0.5 cms^{-1}
Sampling interval	30 min	30 min
ADCP Depth	8.8 m	8.8 m
Depth first good cell	15 m	15 m
Depth last good cell	89 m	
Temperature:		
Instrument	Thermistor chain	Temperature loggers
Sampling interval	1 hour	15 min
Depths	13-53 m, 4 m intervals	13-29 m, 4 m intervals
Available Data		
Currents	06/18/97-09/16/97	06/18/97-06/24/97
Temperature	06/18/97-09/16/97	06/18/97-09/16/97

An ADCP transmits acoustic pulses from a Janus configured four-transducer assembly and receives return echoes reflected from scatterers in the water, such as plankton, sediment, or bubbles. Current velocities are determined using the Doppler principle. Two acoustic beams are required to compute one horizontal current component and one vertical velocity. A second pair of transducers computes the other horizontal component and a second vertical velocity. The difference between the two independent measurements of vertical velocity is termed the error velocity and is a useful data quality indicator. Nonzero error velocity values indicate either that the equipment is malfunctioning or that there is horizontal nonuniformity in the water. Range-gating the echo signal into successive segments are processed independently thereby producing a profile. Parameters routinely recorded by ADCPs are vertical profiles of horizontal velocity, vertical velocity, error velocity, and echo intensity. Vertical velocity accuracy is not as readily verifiable because of the small magnitudes and difficulty of making validating measurements and have not been included in this report. Comparisons of ADCPs and conventional mechanical current meters, for example Savonius rotor meters, show very good correlation of horizontal velocities (Miller and Saylor, 1993; Appell et al., 1991; Pettigrew et al., 1986).

Echo intensity, a measure of the returning signal strength reflected by suspended particles, is generally reported in terms of the volume scattering strength (Medwin and Clay, 1998).

$$S_v = 10\log_{10}(I_R / I_I)$$

where S_v is the volume backscattering strength in dB, I_R is the returned intensity, and I_I the incident or transmitted energy. Received backscatter power is a nonlinear function of the strength of the transmitted power, properties of the receivers, the loss of energy due to sound absorption, beam spreading, and the effective area of the reflecting particles. Obtaining absolute backscatter values, that is, values that are instrument independent, require that each unit go through extensive calibration procedures, procedures that have not been routinely available.

Using a working version of the sonar equation (Deines, 1999) and 'typical' values for strength of the transmitted power and properties of the receivers characteristic of the WH-ADCP, the echo intensity output was adjusted for power attenuation losses due to beam spreading and water absorption.

The ADCP current and temperature data are contained in ASCII and MS Excel files and can be found at: ftp://ftp.glerl.noaa.gov/publications/tech_reports/glerl-116. A data description is given in Appendix II.

Contour plots of data collected at mooring C5 are shown in Figure 4.

RESULTS AND DISCUSSION

Prior to this effort, there was no trapping done in Grand Traverse Bay, thus we relied on our 15-year record of sampling in reasonably similar environments for selecting locations for trap placement. Long-term average mass fluxes measured from 1978 to 1992 at a 100 m deep station, 25 km offshore in southeastern Lake Michigan exhibit profiles of mass flux with an exponential increase toward the bottom. From late December through early June, Lake Michigan is virtually isothermal and well mixed. Average fluxes during this period are high throughout the water column, but there is clear evidence of a benthic nepheloid layer (BNL). During the stratified period (June-December), the upper half of the water column becomes isolated from the large inventory of materials in the sediments, although episodic mixing does occur during upwellings. A BNL is still clearly evident from the mass flux profile.

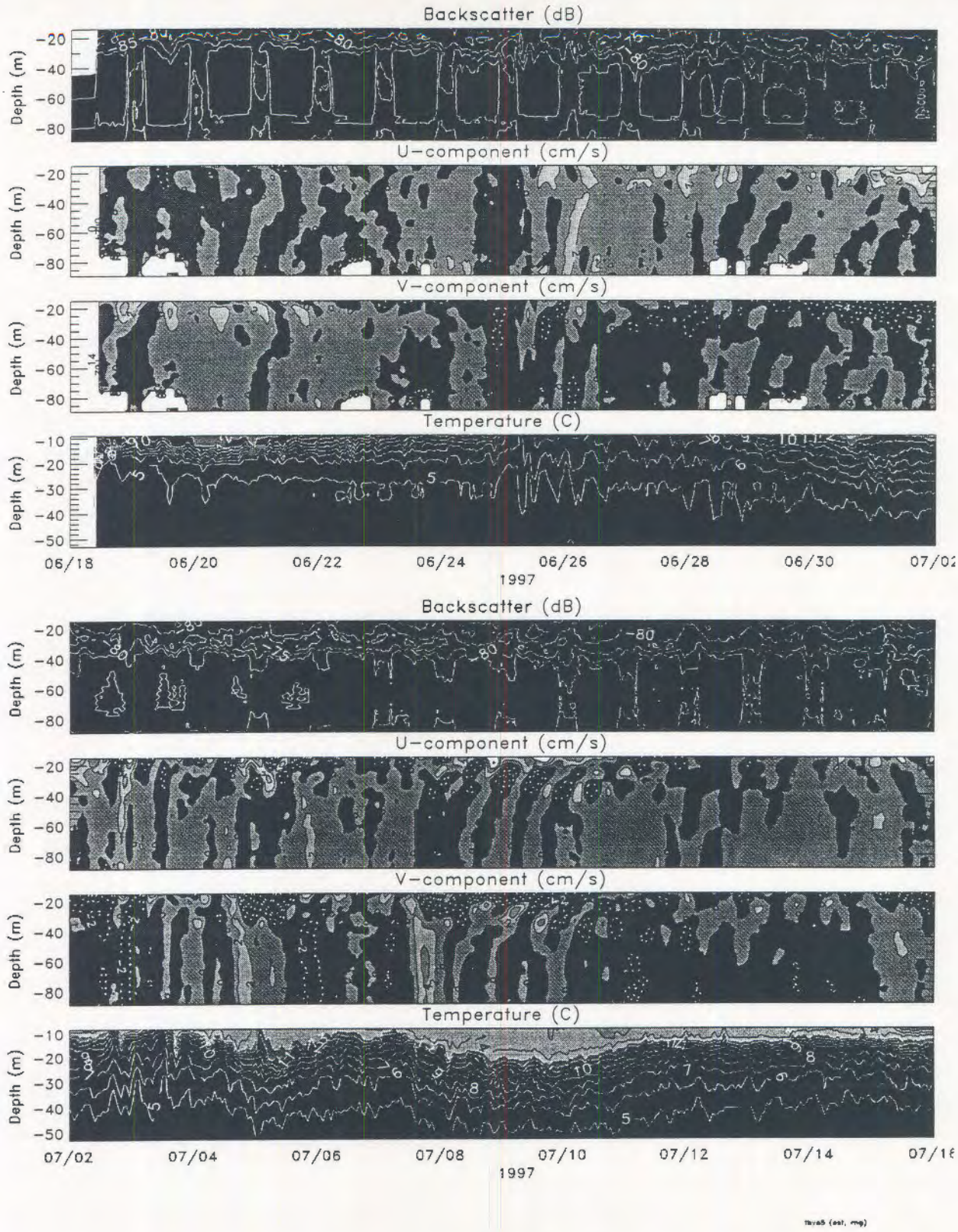

Figure 4. Contours of backscatter strength, U and V current components, and water temperature from mooring C5. Positive U is towards the east; positive V towards the north. The white areas in the U and V panels in June indicates that the acoustic backscatter was insufficient to compute a credible current velocity.

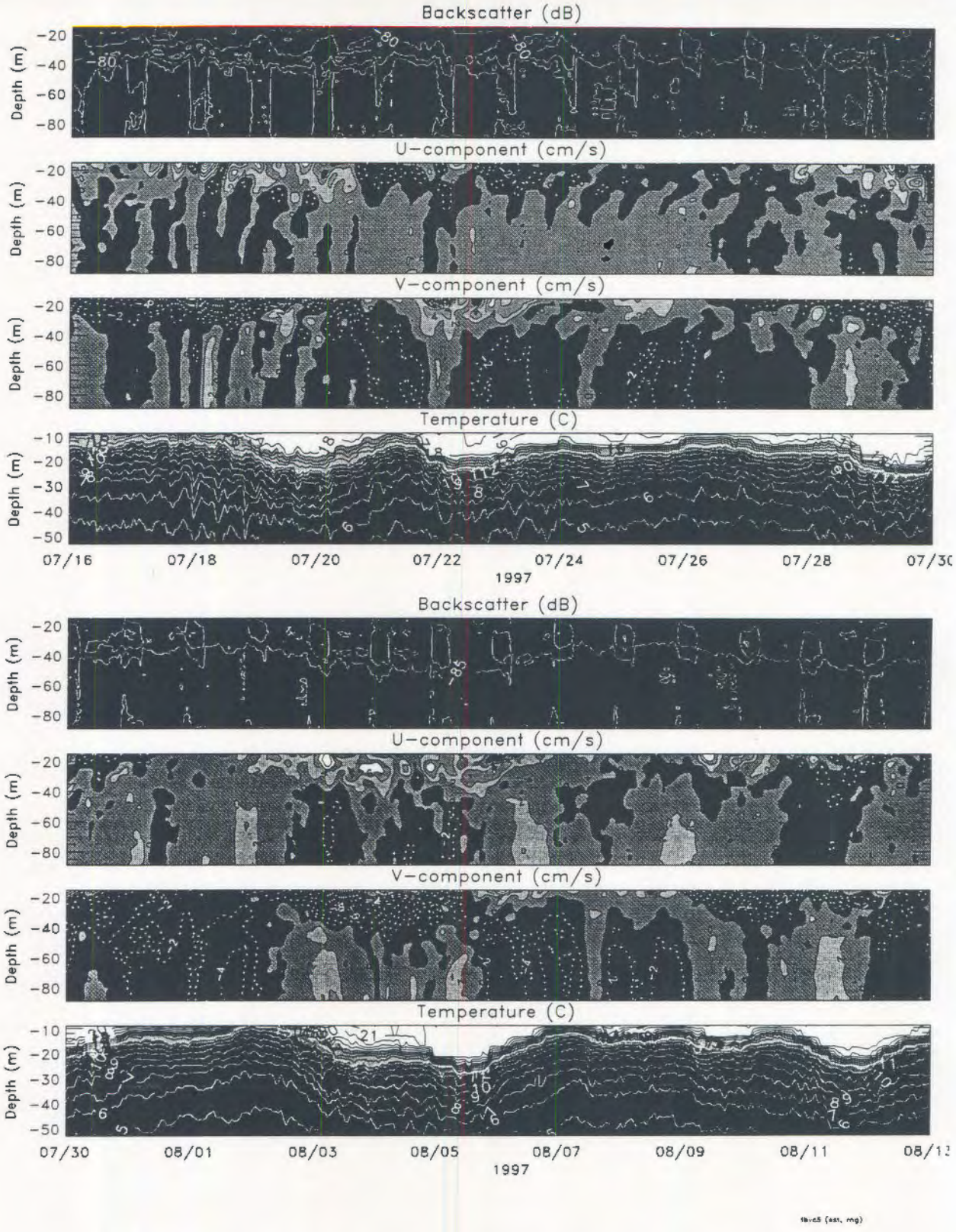

Figure 4 (cont). Contours of backscatter strength, U and V current components, and water temperature from mooring C5. Positive U is towards the east; positive V towards the north. The white areas in the U and V panels in June indicates that the acoustic backscatter was insufficient to compute a credible current velocity.

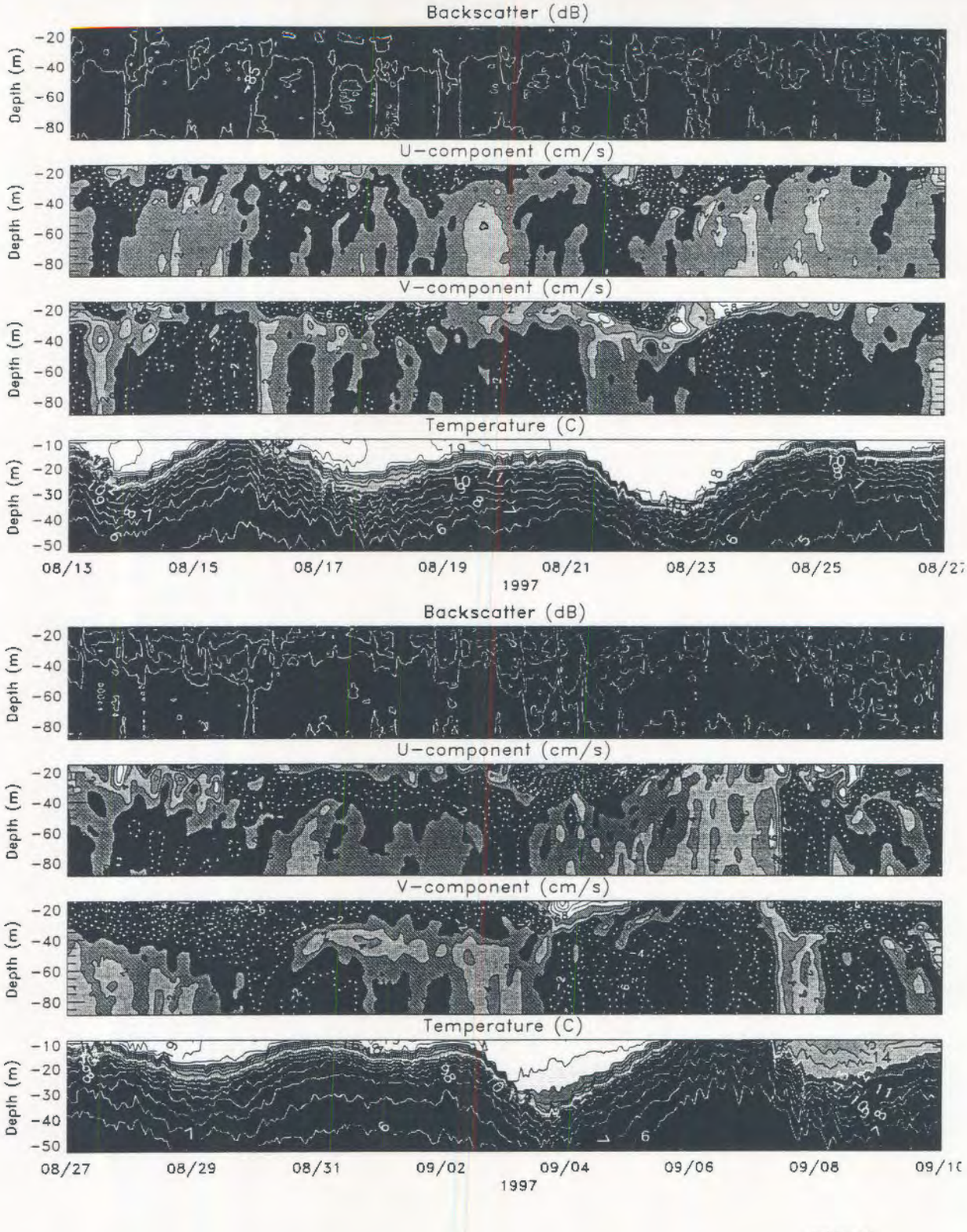

Figure 4 (cont). Contours of backscatter strength, U and V current components, and water temperature from mooring C5. Positive U is towards the east; positive V towards the north. The white areas in the U and V panels in June indicates that the acoustic backscatter was insufficient to compute a credible current velocity.

All trap data are presented in Appendix 1.

Overall, five (week-long) cruises of the R/V SHENEHON were conducted in Grand Traverse Bay. Co-Principal Investigators and graduate students participated in all cruises, collecting water, particulate, and biological samples as part of their overall sampling strategy. Cruises left Muskegon on 5/5/97, 6/16/97, 9/15/97, 8/31/98, and 8/2/99, stopping overnight in Frankfort and arriving in the bay on the afternoon of the second day.

Results: Spring-Summer 1997

In early May 1997 profiles of non-sequencing traps (4" diameter) were deployed at stations 6, 8, and 9, along with profiles of sequencing and non-sequencing traps at stations 4, 5, and 7 (see Figures 3 and 5). The primary objective of this extensive sampling was to get some preliminary flux data from a system where none had been previously collected.

The non-sequencing trap arrays at stations 6, 8, and 9 were retrieved and redeployed after the onset of thermal stratification, approximately 40 days after deployment, and mass fluxes calculated. All traps were retrieved in mid-September, and sequencing traps were redeployed at stations 5 and 7. Subsamples were distributed for constituent analysis.

Results from the first deployments are displayed in Figure 6 (a and b). Measured fluxes for the unstratified May-June period at stations 6, 8, and 9 were low compared to open Lake Michigan values (average 5 $g/m^2/d$ near the surface), and appeared more like open lake flux profiles during the stratified period when the lake is decoupled from sediment resuspension. All of the profiles exhibit the exponential increase in mass flux near the bottom observed in all Great Lake profiles and attributed to a benthic nepheloid layer. The samples from trap 6 exhibit a peculiar profile -- some sample was lost from the bottom trap during retrieval in June, but the low flux values at 75 m are unexplained at this time.

The sequencing trap mass flux values from relatively shallow (45 m) station 4 were unexpectedly low for the entire spring-summer period (Figure 7). The three samples immediately after the onset of stratification were the highest recorded for the entire period of deployment and will be examined for biogenic silica. This may be the spring bloom in the southeastern portion of the bay.

There was a small peak in mass fluxes at the near-surface of station 5 and 7 in late spring, but except for the initial interval immediately after deployment, the qualitative pattern of mass fluxes were not synchronous within the eastern arm of the bay. Near-bottom fluxes were several times higher at station 7 than at station 5 and may point to a region of sediment focusing near station 7.

Results: Sequencing traps 1997-1999

Two sequencing traps were deployed in mid-September 1997 at station 5 (30 and 91 m) and three at station 7 (15, 30, and 115 m). Trap sampling intervals were set at 15 days. These stations were selected by collaborators as the primary water column stations and were sampled approximately monthly during the 1997-98 season. These traps were retrieved and others redeployed at 30 m below the surface at stations 5, 7, 8, and 9 in early September 1998. These final deployments had collection intervals of 12-15 days and were retrieved in early August 1999. All of the successful samples are illustrated in Figure 8.

These deployments have provided 2 complete years of mass fluxes and samples for analyses from 30 m below the surface at stations 5 and 7 in the eastern and nearly 1 full year from the same depth in the western arm (station 9). There is clear evidence in these records of strong resuspension during the unstratified periods in the 2 years. These fluxes are substantially higher at the more southern station (5) than at station 7. The qualitative flux patterns do not appear to be well synchronized between these two stations implying a complex transport of particu-

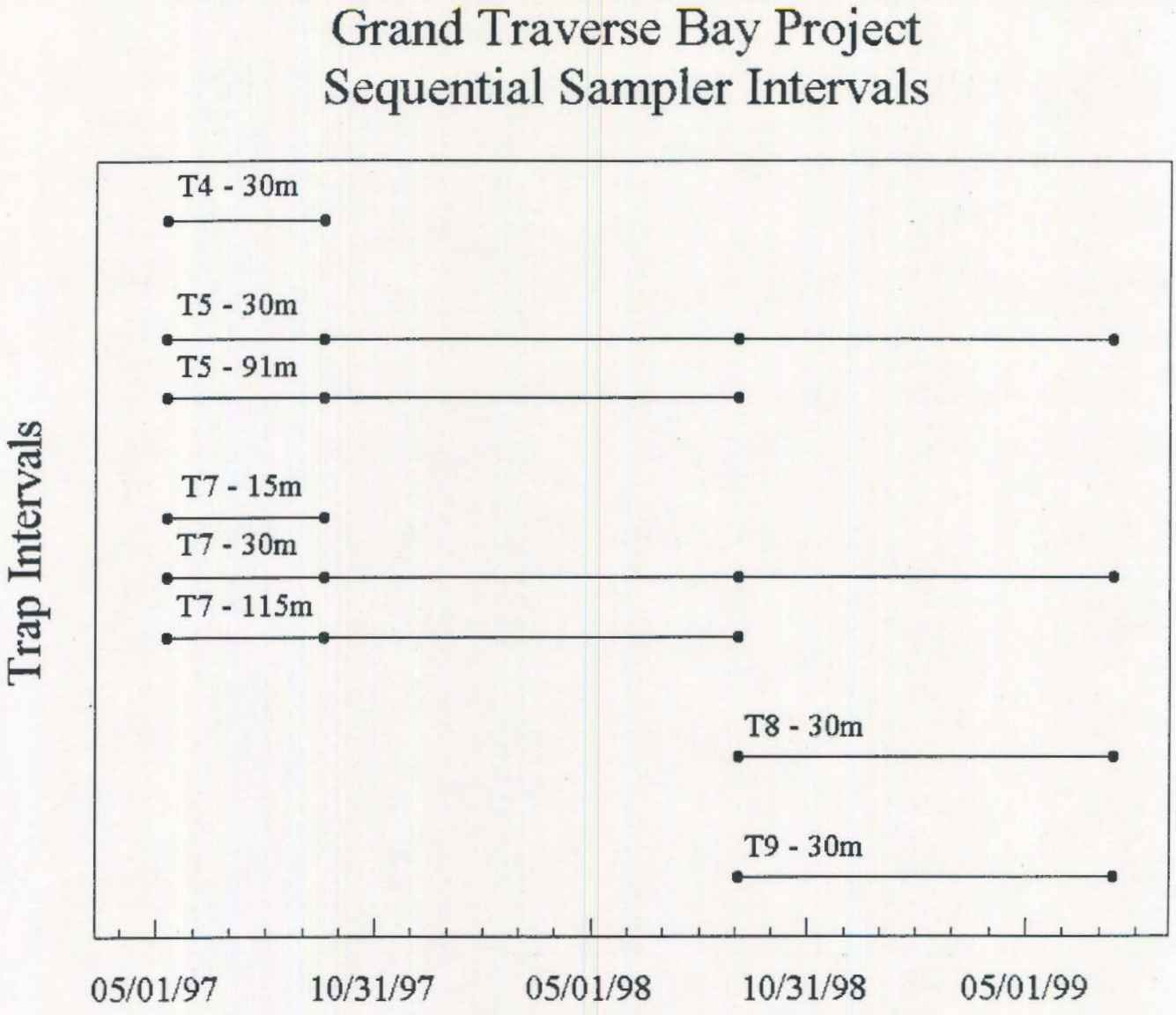

Figure 5.--Sequencing trap deployment schedules. Symbols represent times of deployment and retrieval.

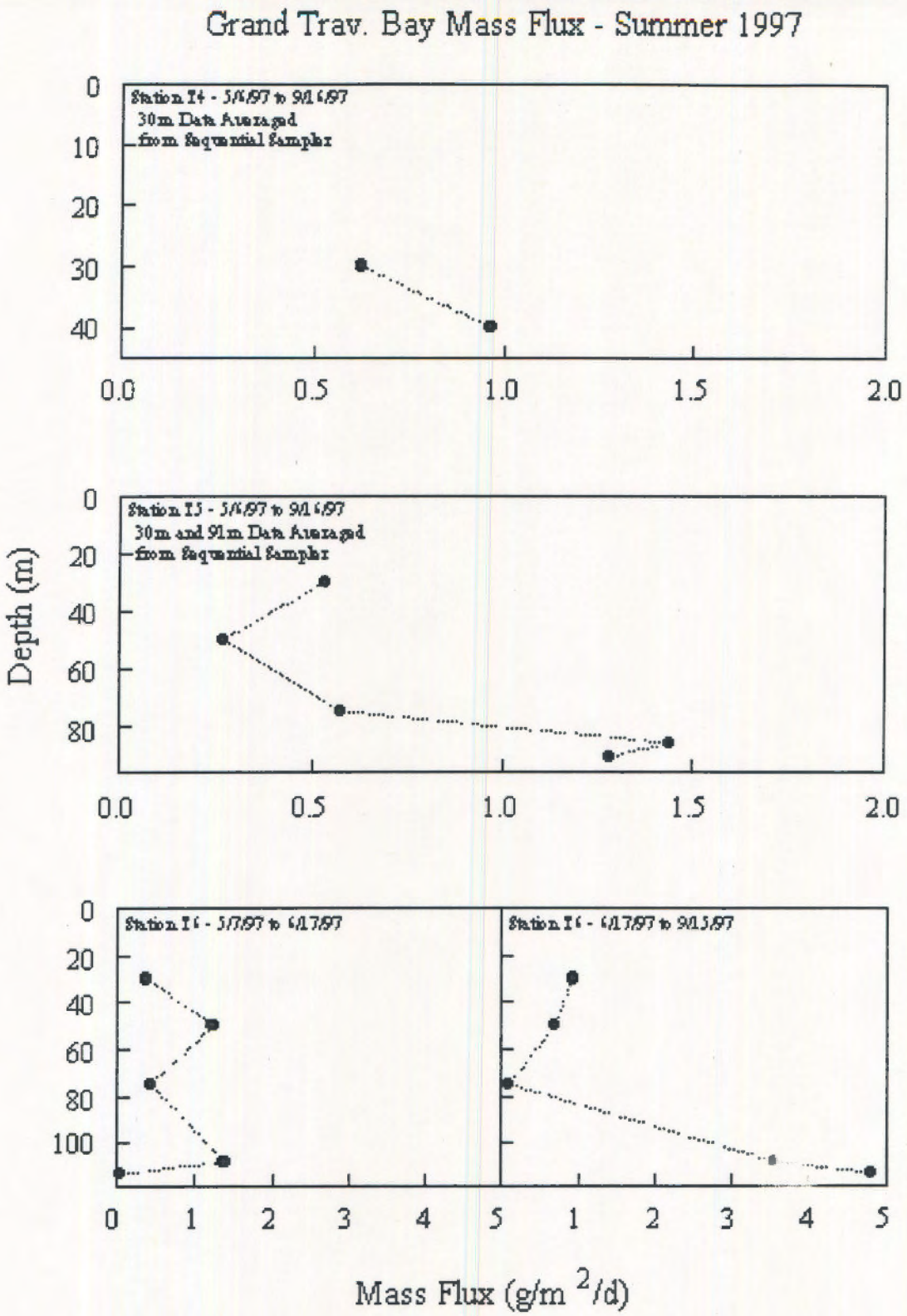

FIGURE 6.-- a) Mass flux profiles for stations 4, 5, and 6 for the spring-summer of 1997.

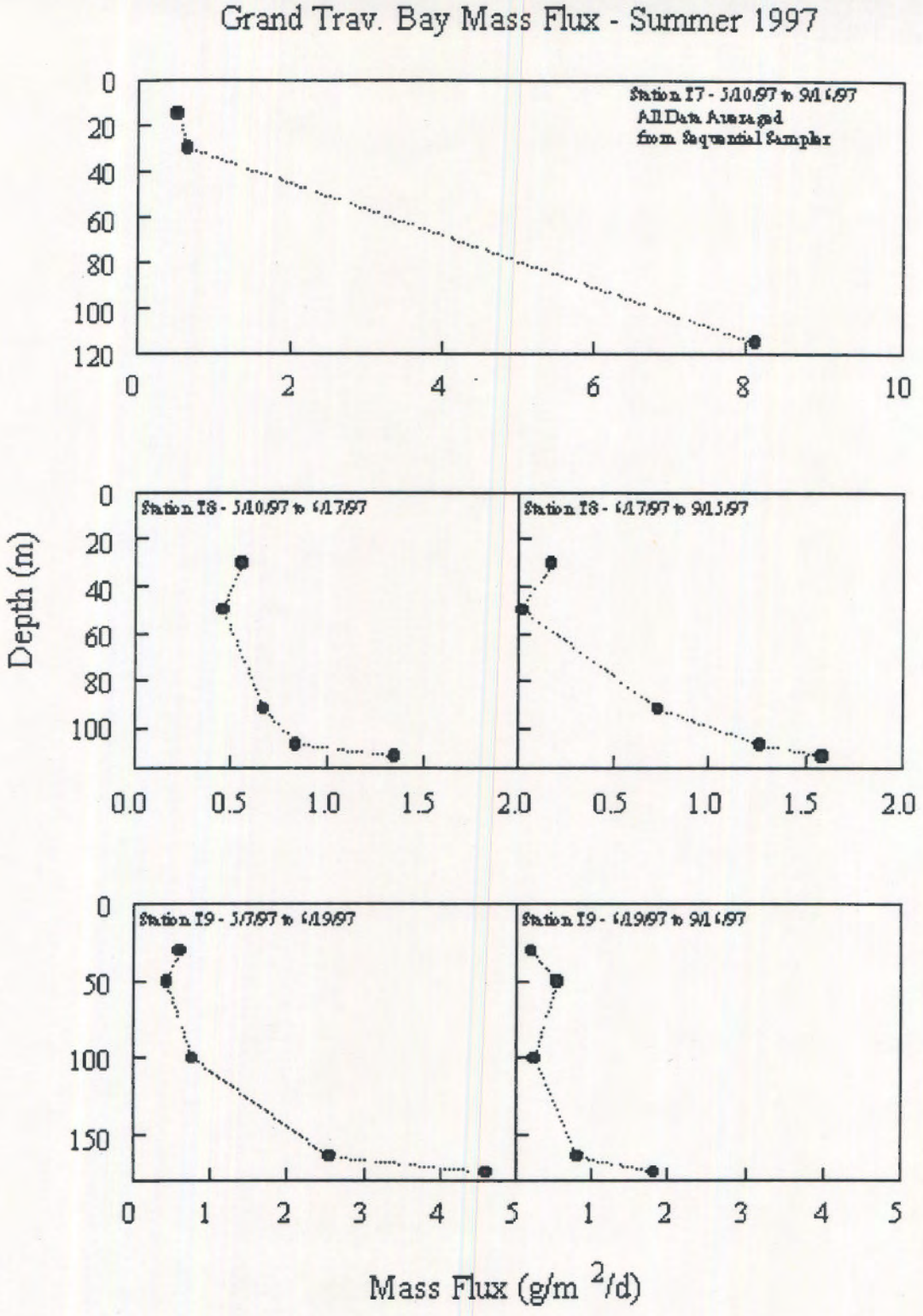

FIGURE 6.--b) Mass flux profiles for stations 7, 8, and 9 for the same period. Split panels represent two deployments, the data for stations 4,5, and 7 are a combination of non-sequencing traps and sequencing traps (see appendix I).

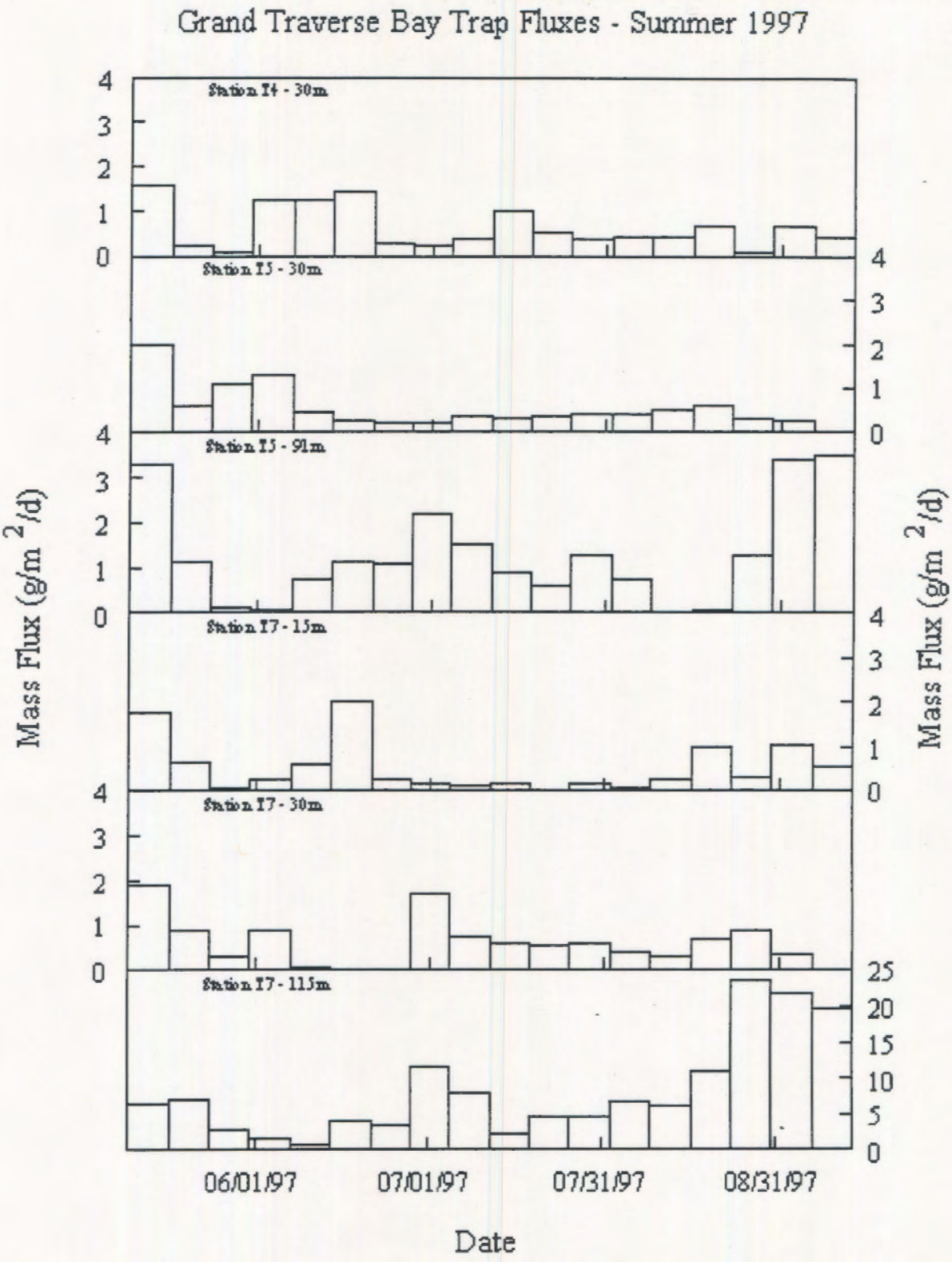

Figure 7.-- Mass fluxes measured at the sequencing traps from stations 4, 5, and 7. All trap intervals were 7 days during these deployments.

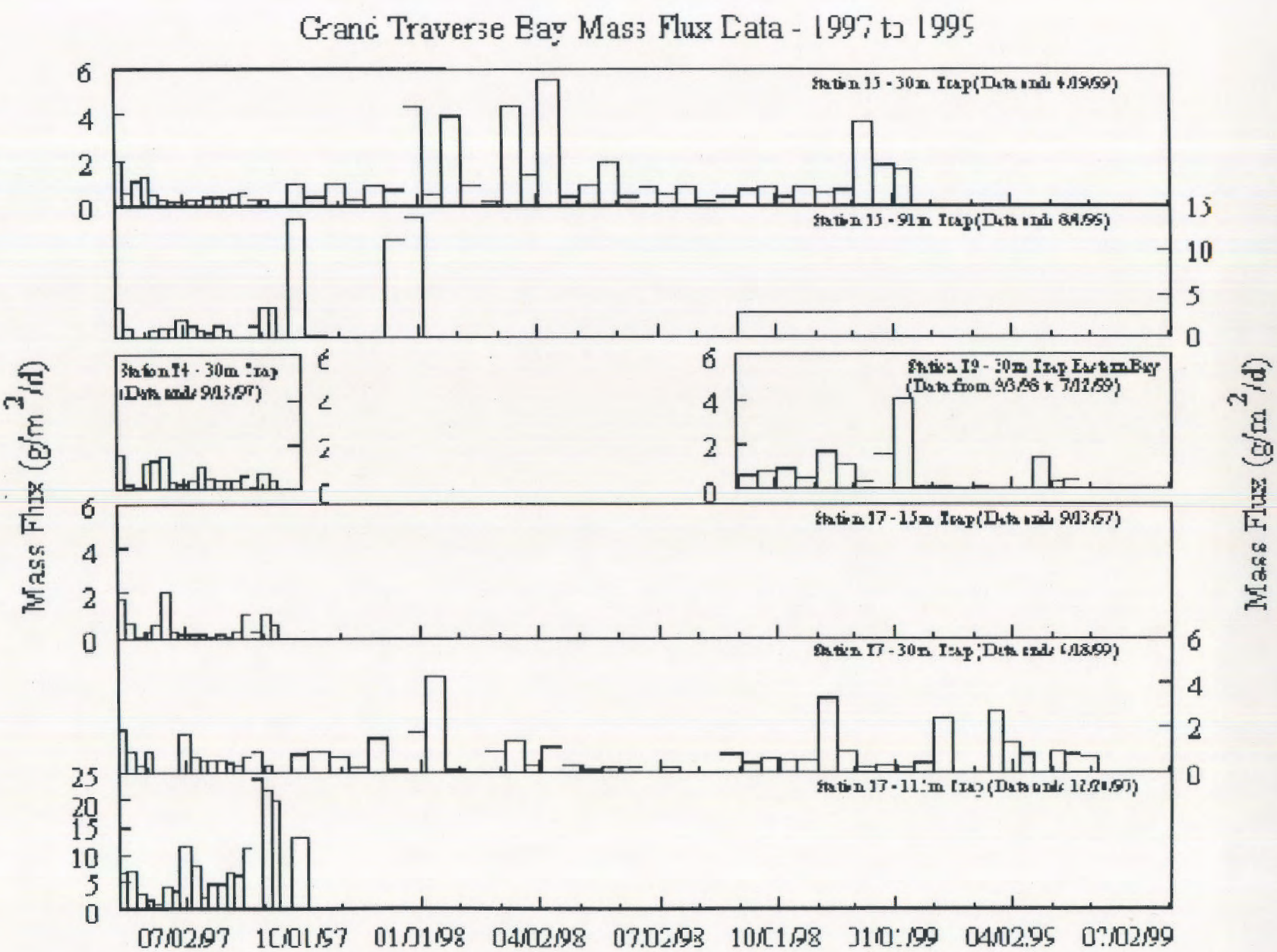

Figure 8.–Mass fluxes at all sequencing trap sites for the entire period of deployment, May 1997 through August 1999.

late matter within the western arm of the bay. Peak mass fluxes at station 9, in the eastern arm, are about the same magnitude during the unstratified period, but not well correlated temporally.

Our results clearly support the hypothesis that there is significant sediment-water exchange of chemical constituents during the unstratified periods when massive sediment resuspension events occur.

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Appendix 1
Values of all trap data collected in Grand Traverse Bay, Lake Michigan during 1997–1999.

Data are contained in both ASCII and MS Excel files at:
ftp://ftp.glerl.noaa.gov/publications/tech_reports/glerl-116.

Appendix 2
Acoustic Doppler Current Profiler (ADCP) current meter and temperature data collected in Grand Traverse Bay, Lake Michigan during summer 1997.

Data are contained in both ASCII and MS Excel files at:
ftp://ftp.glerl.noaa.gov/publications/tech_reports/glerl-116.
File format is shown below.

ADCP current velocity and backscatter data mooring C5 (hourly data):
gtb_c5_97.txt and gtb_c5_97a.txt
Header: rec #, year, mon, day, hour(est), min, water temp(C)
$Depth_1$(m), U_1(cm/s), V_1(cm/s), $Backscatter_1$(dB)
$Depth_2$(m), U_2(cm/s), V_2(cm/s), $Backscatter_2$(dB)
... ...
... ...
$Depth_n$(m), U_n(cm/s), V_n(cm/s), $Backscatter_n$(dB)
Header: rec #, year, mon, day, hour, min, water temp(C)
$Depth_1$(m), U_1(cm/s), V_1(cm/s), $Backscatter_1$(dB)
$Depth_2$(m), U_2(cm/s), V_2(cm/s), $Backscatter_2$(dB)
... ...
... ...
$Depth_n$(m), U_n(cm/s), V_n(cm/s), $Backscatter_n$(dB)
Etc.
(Missing data –999.0)

Water temperature data mooring C5 (hourly data; the ADCP temperatures at the 9 m depth are included):
gtb_c5allt.txt
Information header
Day-of-yr, time(est), year, rec #, id #, watertemp(1-12) (deg C)
(Missing data = -0.45)

Water temperature data mooring C7 (30-minute data; the ADCP temperatures at the 9m depth are included):
gtb_c7allt.txt
Information header
Day-of-yr, time(est), year, rec #, water temp(1-6) (deg C)